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The oxygen analysis of solid wastes is one of the important ultimate analysis necessary to determine: the efficiency of operation of an incinerator, the design of furnaces for incineration, and a complete materials balance of incoming and outgoing material. The oxygen content of solid wastes samples must be known if their calorific values are to be calculated from ultimate analyses.

The two new formulas for calculating total oxygen content in solid wastes samples correlate data from as many as eight different analyses. These eight components are: total carbon, carbonate carbon in total sample, carbonate carbon in ash from volatile at 600C, total hydrogen, total nitrogen, total sulfur, total chlorine, and a volatile at 600C or at 950C value. The oxygen method, described here, deals with the procedures for the eight related components.

The new formulas for oxygen concentrations still have the errors inherent in the other analyses, particularly the volatile analysis; however, they do take into account carbonate oxygen which could cause the greatest inaccuracy in total oxygen data for solid wastes samples. The recommended procedure for determining carbonate oxygen and organically-bonded oxygen is: first determine carbon carbon, multiply this answer by four for carbonate oxygen, and then obtain the organically-bonded oxygen content by substracting the carbonate oxygen value from the total oxygen concentration.

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MATHEMATICAL DETERMINATION

OF TOTAL OXYGEN

IN SOLID WASTES

A Solid Waste Research
Open-File Report (RS-03-68-17)

written by

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U.S. ENVIRONMENTAL PROTECTION AGENCY
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1971

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DISCUSSION

The oxygen analysis of solid wastes is one of the important ultimate analysis necessary to determine: the efficiency of operation of an incinerator, the design of furnaces for incineration, and a complete materials balance of incoming and outgoing material. The oxygen content of solid wastes samples must be known if their calorific values are to be calculated from ultimate analyses.

The direct approach of determining oxygen content in solid wastes would involve much time and expense. Although a direct method is more exacting, an indirect approach[1] employing a formula with ultimate analyses and an ash value is presently being used for each coal or coke sample, and this indirect approach can be applied to solid wastes samples. However, since the oxygen-formula applies to coal and coke samples and is related to a particular method of ashing[2], the formula must be modified before it can be applied to solid wastes samples.

The modified method[3] is actually two oxygen-formulas. Each of which depends upon the ashing technique employed. One procedure of ashing is the standard method for solid wastes samples[4] which involves heating the sample to 600C, but requires testing for the decomposition of carbonates. The other ashing technique is to weigh the ash from the carbon-hydrogen method.[5] Although either ashing technique may be used for this method, ashing as part of the carbon-hydrogen method is recommended because the extension of the carbon-hydrogen procedure (weighing the residue and correcting for oxidation of combustion aid) requires very little extra time or effect and eliminates the need for determining amount of carbonate decomposition.

The two new formulas for calculating total oxygen content in solid wastes samples correlate data from as many as eight different analyses. These eight components are: total carbon, carbonate carbon in total sample[6], carbonate carbon in ash from volatile at 600C, total hydrogen, total nitrogen[7], total sulfur[8,9], total chlorine[10], and a volatile at 600C or at 950C value. The oxygen method, described herein, deals with the procedures for the eight related components.

The new formulas for oxygen concentrations still have the errors inherent in the other analyses, particularly the volatile analysis; however, they do take into account carbonate oxygen which could cause the greatest inaccuracy in total oxygen data for solid wastes samples.

Total oxygen content of a solid waste sample is defined as either all the oxygen contained in the volatile-at-600C portion plus the inorganically combined oxygen of carbonates in the sample or all the oxygen contained in the volatile-at-950C portion. This total oxygen value does not include oxygen which is already combined with metals or silicon.

The recommended procedure for determining carbonate oxygen and organically-bonded oxygen is: first determine carbonate carbon, multiply this answer by four for carbonate oxygen, and then obtain the organically-bonded oxygen content by subtracting the carbonate oxygen value from the total oxygen concentration.

APPARATUS

This procedure requires no apparatus other than what is needed for the eight different analyses that must be performed to obtain the data for this method.

REAGENTS

No reagents are necessary for this analysis. Reagents are needed for the eight correlated methods and are mentioned in the appropriate method.

SAFETY PRECAUTIONS

No safety hazards exist in this procedure. Safety precautions necessary in related methods have been discussed in those methods.

SAMPLE PREPARATION

Preparation of solid wastes samples are discussed in the carbon-hydrogen method and elsewhere.[11] Therefore, sample preparation techniques are not repeated in this method.

PROCEDURE

Carbon-Hydrogen Analyses

Procedure	Comments
1. Determine total carbon and hydrogen contents of solid wastes samples by the method developed particularly for solid wastes samples. (See reference #5)	1. With this method larger sample portions are analyzed than with similar methods.

Carbonate Carbon Analysis

Procedure	Comments
1. Determine carbonate carbon content of solid wastes samples. by the method developed particularly for solid wastes samples. (See reference #6)	1. a) This analysis is needed for the carbonate oxygen content of the sample. b) This same method is employed to find carbonate carbon in ash from volatile-at-600C analysis.

Nitrogen Analysis

Procedure

1. Nitrogen content of solid wastes samples may be determined by an AOAC method. (See reference #7).
2. Nitrogen content of incinerator raw refuse, incinerator combustible-residue, and compost samples may be estimated to be 0.75%. (See reference #3).
3. Nitrogen content of incinerator noncombustible-residue samples and incinerator fly ash samples may be estimated to be 0.15% (See reference #3).

Comments

1. This method is the one most commonly used for solid wastes samples.
2. This estimate is the average nitrogen content of twelve raw refuse samples. These nitrogen contents ranged from 0.49% to 1.42%.
3. This estimate is the average nitrogen content of nine noncombustible-residue samples. The nitrogen concentrations ranged from 0.04% to 0.31%.

Sulfur Analysis

Procedure

1. Sulfur content of solid wastes samples may be determined by an ASTM method. (See references #8 and #9).

Comments

1. a) This method is the one most commonly used for solid wastes samples. (See reference #8).

   b) The related bomb-combustion method was developed especially for solid wastes samples. (See reference #9).

2. Sulfur content of solid wastes samples (raw refuse, incinerator residue, incinerator fly ash, and compost) may be estimated to be 0.20%. (See reference #3)	2. The exact average sulfur content of twenty-one samples (twelve raw refuse and nine noncombustible-residue samples) was 0.19%. The sulfur concentration ranged from 0.10% to 0.37%.

Chlorine Analysis

Procedure	Comments
1. Chlorine content of solid wastes samples may be determined by an AOAC method. (See reference #10)	1. This method is the one most commonly used for solid wastes samples.
2. Chlorine content of incinerator raw refuse, incinerator combustible-residue, and compost samples may be estimated to be 0.50%. (See reference #3)	2. The exact average chlorine content of twelve raw refuse samples was 0.52%. The chlorine concentrations ranged from 0.29% to 1.10%.
3. Chlorine content of incinerator noncombustible-residue samples and incinerator fly ash samples may be estimated to be 0.10%. (See reference #3)	3. The exact average chlorine content of nine noncombustible-residue samples was 0.11%. The chlorine concentrations ranged from 0.06% to 0.15%.

Voltaile-Ash Analysis

At 600 C

Procedure	Comments
1. The volatile or ash at 600 C content of solid wastes samples may be determined by an APWA method. (See references #3 and #4)	1. a) This method is the one most commonly used for solid wastes samples, but not preferred. b) Although not commonly used in solid wastes management, the term L.O.I. (loss-on-ignition) at 600 C is more meaningful than the term volatiles. c) Data obtained with this method does not vary with age of samples (up to two years old). d) Reproducibility of data is affected by large amounts of carbonates present in the sample.
2. Determine carbonate carbon content of the ash from the volatile analysis. (See Carbonate Carbon Analysis)	2. Carbonate carbon analysis is needed in order to determine the degree of decomposition of carbonate in the volatile at 600 C analysis.

At 950 C

Procedure	Comments
1. The volatile or ash at 950 C content of solid wastes samples may be determined either by muffling as in the APWA method for 600 C or by weighing the ash from the carbon-hydrogen method. (See references #3, #4, and #5)	1. a) This analysis (volatiles at 950 C) is not the most commonly used for solid wastes samples, but is preferred because it is easily obtained with the carbon-hydrogen method and decomposition of carbonates may be considered to be 100% at 950 C. b) Although not commonly used in solid wastes management, the term L.O.I. (loss-on-ignition) at 950 C is more meaningful than the term volatiles.
2. If the ash data is obtained from the carbon-hydrogen method, the ash value must be corrected for the increase in weight of the combustion aid (iron clips) used. The average percent increase in weight of the combustion aid is 21.8%.	2. a) Since the ash may contain calcium oxide which easily absorbs moisture, the ash from the carbon-hydrogen must be kept in a desiccator until weighed. b) This average percent-weight-increase was determined

from ten analyses with iron clips. The weights of iron clips varied from 0.1957 g to 0.4192 g. The percent-weight-increase varied from 17.7% to 24.6%.

STANDARDIZATION AND CALIBRATION

No standardization and calibration are required for the total oxygen analysis. These techniques are disclosed in methods associated with this procedure for total oxygen content of solid wastes samples.

CALCULATIONS

1. Formula for total % oxygen from volatiles at 600 C:

$$\%O = V_1-(\frac{44}{12})\ (C_i)\ (C_{id})-C_o-H-N-S-Cl+(\frac{4}{1})\ (C_i)$$

Where:

- % = the total percent by weight
- O = the element oxygen
- V_1 = the percent of sample that volatilized at 600 C
- $\frac{44}{12}$ = the molar ratio of carbon dioxide to carbon
- C_i = the percent of inorganically bonded (carbonate) elemental carbon
- C_{id} = the decimal fraction of the amount of carbonate carbon which decomposed in the volatile at 600 C analysis
- C_o = the percent of organically bonded elemental carbon
- H = the total percent of the element hydrogen
- N = the total percent of the element nitrogen
- S = the total percent of the element sulfur

Cl = the total percent of the element chlorine

$\frac{4}{T}$ = the molar ratio of oxygen to carbon in carbonates

NOTE: a) N, S, and Cl may be estimated if not actually determined.

b) All results are on a dry basis.

2. Formula for total % oxygen from volatiles at 950 C:

$$\%O = V_2 - C_t - H - N - S - Cl$$

Where: % = the total percent by weight

O = the element oxygen

V_2 = the percent of sample that volatilized at 950 C

C_t = the total percent of the element carbon

NOTE: a) N, S, and Cl may be estimated if not actually determined.

b) All results are on a dry basis.

3. Conversion of carbonate carbon analysis on ash from volatile at 600 C to original sample basis:

$$\% C_{ic} = (C_{ia})(A)$$

Where: % = the percent by weight

C_{ic} = the carbonate carbon in ash at 600 C, on original sample basis (before ashing)

C_{ia} = the percent of carbonate carbon in ash at 600 C

A = the decimal fraction of the amount of ash remaining after volatilizing the sample at 600 C

NOTE: All results are on a dry basis

4. Formula for amount of decomposition of carbonates during the volatile at 600 C analysis:

$$\% C_{id} = \frac{(C_i - C_{ic})(100)}{C_i}$$

NOTE: All results are on a dry basis.

5. Conversion of data from a wet basis to a dry basis:

$$\% X_d = (100)(\% X_w) \div (100-m)$$

Where: % = the percent by weight

X_d = the ingredient on a dry basis, except volatiles

X_w = the ingredient on a wet basis, except volatiles

m = the percent of moisture (loss-at-105 C)

Volatiles only:

$$\% V_d = (V_w - m) \div (100-m)$$

Where: % = the percent by weight

V_d = the volatile portion of the sample, dry basis

V_w = the percent volatile portion of the sample, wet basis

6. Formula for % carbonate oxygen:

$$\% O_c = (\tfrac{4}{7})(C_i)$$

Where: % = the percent by weight

O_c = inorganically bonded (carbonate) elemental oxygen

7. Formula for % organically bonded oxygen:

$$\% O_o = \% O - \% O_c$$

Where: % = the percent by weight

O_o = organically bonded elemental oxygen

METHOD EVALUATION

The accuracy of this method is dependent upon the accuracy of the related analyses and the care in removing metals during sample preparation.

The variance in the oxygen results is a composite of the precision of the associated analyses. The largest deviation from the average value exist usually in the volatile analysis; therefore, reproducibility of the

volatile data is what mostly determines precision of the oxygen data. Since the carbonate content of a sample affects the repeatability of the volatile at 600 C analysis, the oxygen data of samples high in carbonate content can be expected to show poor precision if the data was obtained with the volatile at 600 C analysis.

An inspection of past data indicates the oxygen value could, at most, vary one or two actual precent from the average. This is well within limits of requirements for an estimated oxygen value of solid wastes samples.

The time required to perform the calculations for the oxygen value is trivial, but the related laboratory analyses required are very time consuming; however, such analyses are generally not performed for just an oxygen value. The breakdown of total carbon data into organic and carbonate carbon and the decomposition of carbonates in the volatile at 600 analysis are necessary information for calculating oxygen values, but the concepts have also been useful in better understanding the nature of solid wastes samples and the analytical tests performed on them.

REFERENCES

1. American Society for Testing Materials. Oxygen. In 1969 Book of ASTM standards; including tentatives. pt. 19. D 271-68, sect. 42. Philadelphia, 1969. p. 35.

2. American Society for Testing Materials. Ash. In 1969 Book of ASTM standards; including tentatives. pt. 19. D 271-68, sect. 10-12. Philadelphia, 1969. p. 19-20.

3. Wilson, Donald L. Formulas (Incorporating Decomposition of Carbonates at 600 C) for the Determination of Total Oxygen in Solid Wastes. Solid Waste Management Office. (In preparation.)

4. American Public Works Association. Test for Volatile Solids and Ash. In Municipal refuse disposal. 3d. ed. Chicago, Public Administration Service, 1970. p. 393-395.

5. Wilson, Donald L. Laboratory Procedure for the Gravimetric Determination of Carbon and Hydrogen in Solid Wastes. Solid Waste Management Office. 1970.

6. Wilson, Donald L. Laboratory Procedure for the Gravimetric Determination of Carbonate Carbon in Solid Wastes. Solid Waste Management Office. 1971.

7. Horwitz, W. ed. Nitrogen, 2.048-2.075. In Official methods of analysis of the association of official analytical chemists. 11th ed. Washington, D. C., Association of Official Analytical Chemists, 1970. p. 16-20.

8. American Society for Testing Materials. Sulfur by the bomb washing method. In 1969 Book of ASTM standards; including tentatives. pt. 19. D 271-68, sect. 22-23. Philadelphia, 1969. p. 25-26.

9. Wilson, Donald L. Laboratory Procedure for the Total Heat of Combustion Determination in Solid Wastes. Solid Waste Management Office. 1971

10. Horwitz, W. ed. Chlorine official final action, 34.110. In Official methods of analysis of the association of official analytical chemists. 11th ed. Washington, D. C., Association of Official Analytical Chemists, 1970. p. 602.

11. Cohen, Israel R. Laboratory Procedures for the Preparation of Solid Waste Related Materials for Analysis. Solid Waste Management Office (In preparation.)